ENTHALPY-CONCENTRATION DIAGRAMS OF BINARY AQUEOUS MIXTURES OF HYDRAZINE, SODIUM CARBONATE, AND GLYCERINE

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Generally an enthalpy-concentration diagram for a system is prepared for fixed pressure, and to be complete it should include data on the solid, liquid, and vapor phases. Such charts are useful for calculations involving heat balances with accompanying concentration changes. This article outlines the steps in the preparation of a diagram and includes the diagrams for aqueous solutions of hydrazine, sodium carbonate, and glycerine.

Calculation of heat effects accompanying concentration changes in binary solutions can be quickly and easily performed by use of an enthalpy-concentration diagram. Such charts have been called Merkel diagrams after Merkel(*1*), who was the first to give a thermodynamic analysis of the chart and who emphasized the use of it in heat-balance calculations. Zeisberg (*2*) was perhaps the first to compute enthalpy charts of binary mixtures. Ponchon(*3*) and Savarit(*4*) were the first to use the chart for calculating the number of theoretical plates in a rectifying column. Others have contributed to the use of the chart such as Hirsch(*5*), who applied it to single- and multiple-effect evaporators, and McCabe (*6*), who presented the sodium hydroxide-water diagram and reviewed its use in heat-balance calculations. Probably the most complete development of its use was due to Bošnjaković(*7*). He recently applied the diagram to heat-exchange processes in sugar solutions(*8*) and to chemical processes such as ammonia synthesis(*9*). In summary it might be said that the chart may be used to solve any binary-mixture problem involving the first law of thermodynamics. The second law of thermodynamics is involved only in the phase-equilibrium portions of the diagram.

The principles involved in constructing an enthalpy-concentration diagram, given by Dodge(*10*), will be illustrated here by the construction of a diagram for the hydrazine-water system at 1 atm. The construction requires a complete set of thermochemical data for the pure substances and their mixtures over the temperature range desired for the diagram. Lack of such data is the chief reason that there are so few of these diagrams available to industry today. The data required are as follows:

1. Complete enthalpy-temperature data for the pure substances.
2. Heat of solution or dilution data for the binary mixtures.
3. Heat-capacity data for the binary mixtures.
4. Phase-equilibria data for the system if the solid or vapor phases are to be included in the diagram.

As temperatures are frequently measured on the centigrade scale and heat quantities are given in calories in the scientific literature, the most convenient way to report heat quantities or enthalpies is in calories per gram of system or, for engineering use, the equivalent, which is centigrade heat units per pound (C.h.u.). The enthalpy results in these units may be converted to British thermal units per pound by multiplying by 1.8.

Enthalpy of Pure Substances

The enthalpy data for water are available in tabular form from the work of Keenan and Keyes(*11*); the enthalpy data for solid, liquid, and gaseous hydrazine are given in equation form by Audrieth and Ogg (*12*). Generally the enthalpy of a pure substance must be calculated from heat capacity and latent-heat data after suitable enthalpy reference conditions have been selected. The enthalpy reference conditions used here are zero enthalpy for liquid water and solid hydrazine at 0°C. Then the enthalpy of hydrazine liquid at any temperature between its melting point (2.0°C.) and its boiling point (113.5°C.) is given by

$$H_{liq} = \int_0^2 Cp_{solid}\, dt + \lambda_{fusion} + \int_2^t Cp_{liq}\, dt = 95.5 + \int_2^t Cp_{liq} dt \quad (1)$$

and its enthalpy in the vapor region at 1 atm. is given by

$$H_{vapor} = H_{liq}\ (\text{at } 113.5^\circ\ \text{C.}) + \lambda_{vapor} + \int_{113.5}^t Cp_{vapor}\, dt = 485.0 + \int_{113.5}^t Cp_{vapor}\, dt \quad (2)$$

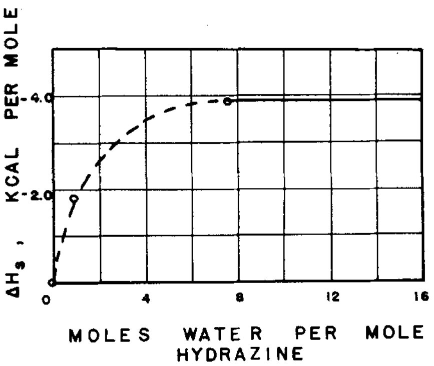


Fig. 1. Heat of Solution of Hydrazine (*12*) in Water at 25° C.; the Value at 7.5 Moles Water/Mole Hydrazine Was Estimated by Analogy with Ammonia.

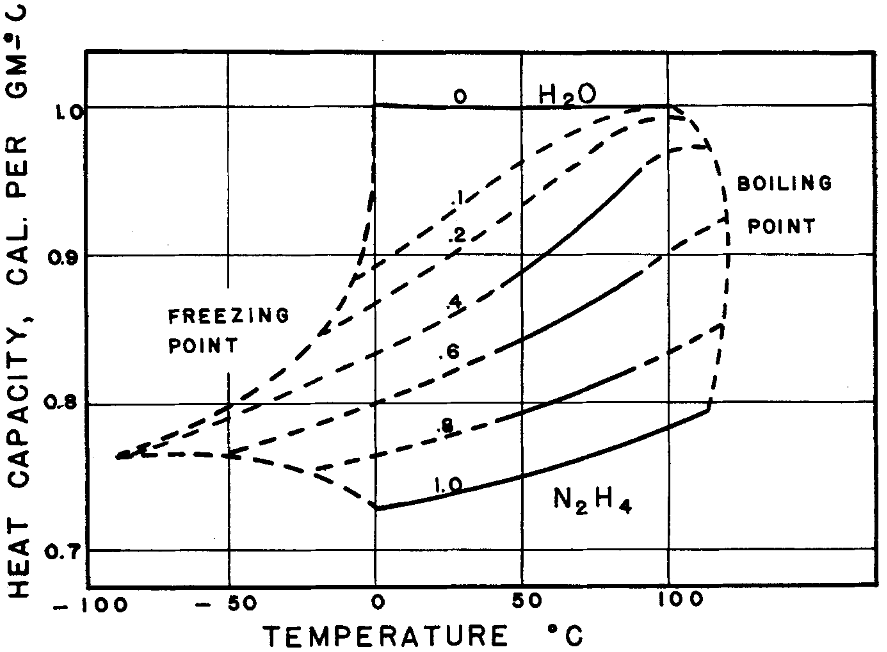
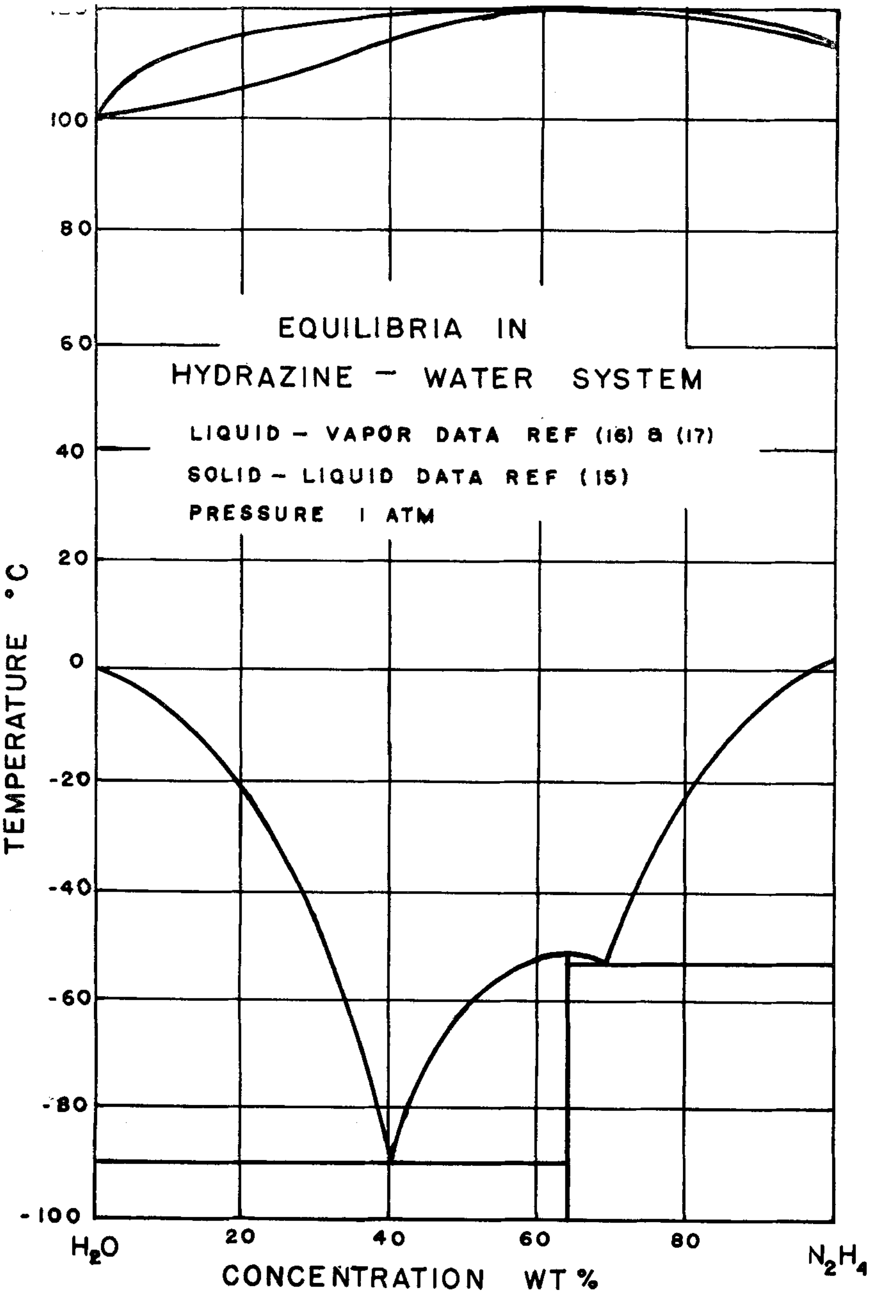


Fig. 2. Heat Capacity of Aqueous Hydrazine at Constant Weight Fractions of Hydrazine. Solid Lines Represent Experimental Data of Sage et al. (*14*).

Fig. 3. Phase Diagram for the Hydrazine-water System at 1 atm. (*15, 16, 17*).



The enthalpy-temperature curves for the pure substances are shown in Figure 5 as the lines in the two *H-t* planes representing pure water and pure hydrazine. Figure 5 is an isometric drawing representing the complete *H-t-x* surface in space.

Since the effect of pressure on the enthalpy of solids, liquids, and gases at low pressures is very small, no attempt has been made here to correct the enthalpy values from the equilibrium vapor pressure of the various phases to 1 atm., the pressure for the diagram.

Heat of Solution or Dilution

The heat of solution of hydrazine in water is given by Audrieth and Ogg(*12*) at 25°C. for infinite dilution and for a concentration of 1 mole water/mole hydrazine. By analogy with ammonia, the hydrazine infinite dilution value is plotted at 7.5 moles water/mole hydrazine, since ammonia has realized its infinite dilution value at this concentration. These data are plotted in Figure 1 and a smooth curve has been put through the points for the purpose of reading intermediate heat-of-solution values for various quantities of water added. The enthalpy of binary mixtures at 25°C. relative to the pure substances having zero enthalpy at 0°C. is given by Equation (3) from Dodge(*10*).

$$H=(1-x)\,H_{H_2O}+x\,H_{N_2H_4}+x\Delta H_{soln} \tag{3}$$

where H is the enthalpy in C.h.u. per pound of binary mixture at 25°C. of weight fraction x in hydrazine and $(1-x)$ in water; H_{H_2O} and $H_{N_2H_4}$ are the enthalpies of water and hydrazine at 25°C. relative to zero values at 0°C. ΔH_{soln} is the heat of solution of hydrazine in water in calories per gram hydrazine (numerically the same as C.h.u. per pound) read from Figure 1 for the various compositions. Thus Equation (3) together with Figure 1 determines the 25°C. isotherm shown on the $H-x$ diagram in Figure (4). If heat-of-dilution data are available, the calculations are very similar. For more details on using heat-of-dilution data the reader is referred to McCabe(*6*) or Dodge(*10*).

Heat Capacity of Binary Mixtures

The enthalpy of a constant-composition mixture at various temperatures relative to the pure substances at the reference conditions is obtained by adding the integral of the heat capacity of the mixture with respect to temperature from 25°C. to t °C. to the enthalpy of that mixture at 25°C., as indicated by Equation (4), where the subscript x indicates constant composition.

$$(H_t)_x = (H_{25})_x + \int_{25}^{t} Cp_x \, dt \qquad (4)$$

Frequently the heat-capacity data are not available over the range of temperature and composition desired, and so it is necessary to use some method of estimating these data. Bushnell, Hughes, and Gilbert(*13*) give heat-capacity data for very dilute aqueous hydrazine solutions at 25°C. and Hough, Mason, and Sage(*14*) have data on various compositions from 40 wt. % to pure hydrazine at several temperatures. These data together with those of pure water were plotted against composition at various constant temperatures, and smooth curves were drawn through the points. Then the heat-capacity-temperature plots at constant composition shown in Figure 2 were made by cross plot from the original data curves. The dotted portions of the curves indicate estimated data. Freezing points and boiling points of the various compositions are also indicated on Figure 2.

Figure 4 shows the complete enthalpy-concentration diagram for hydrazine and water. The 25°C. isotherm, which was established from heat-of-solution data, is the starting point for calculating all the other isotherms on the diagram.

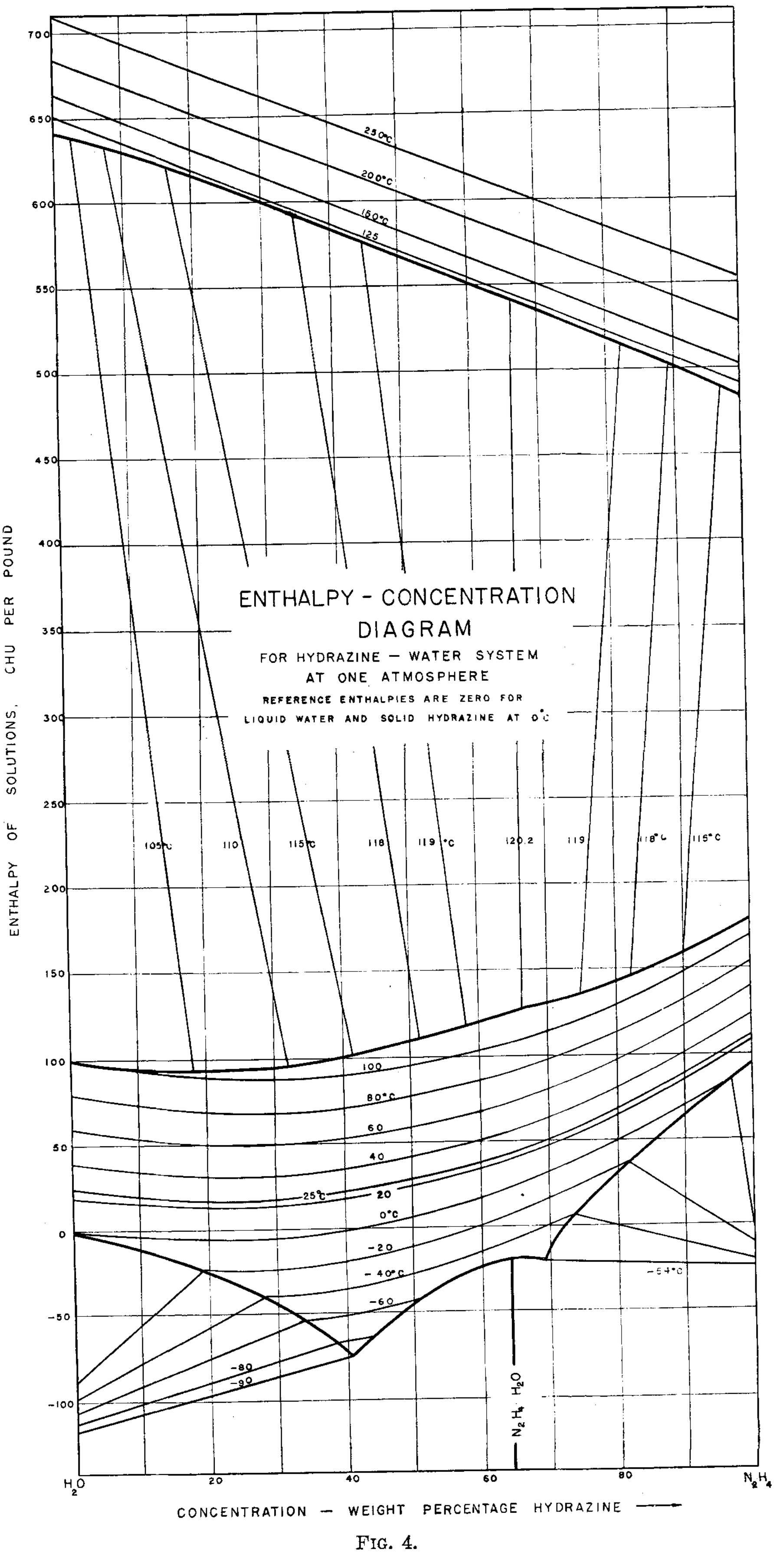


FIG. 4.

Isotherms in the liquid region were established by integrating the heat-capacity data in Figure 2 at constant composition between temperature limits (25° and t°C.) and adding the value of that integral to the enthalpy of that composition at 25°C., as indicated by Equation (4), to obtain the enthalpy of that composition at t°C. The value of the integral is positive for temperatures above 25°C. and negative for isotherms below 25°C. In this manner isotherms were calculated and plotted as shown in Figure (4) for temperatures up to the boiling point and down to the freezing point of the various compositions at 1 atm. pressure. The phase diagram for the system at 1 atm. furnishes data on the equilibrium-phase compositions and transition temperatures.

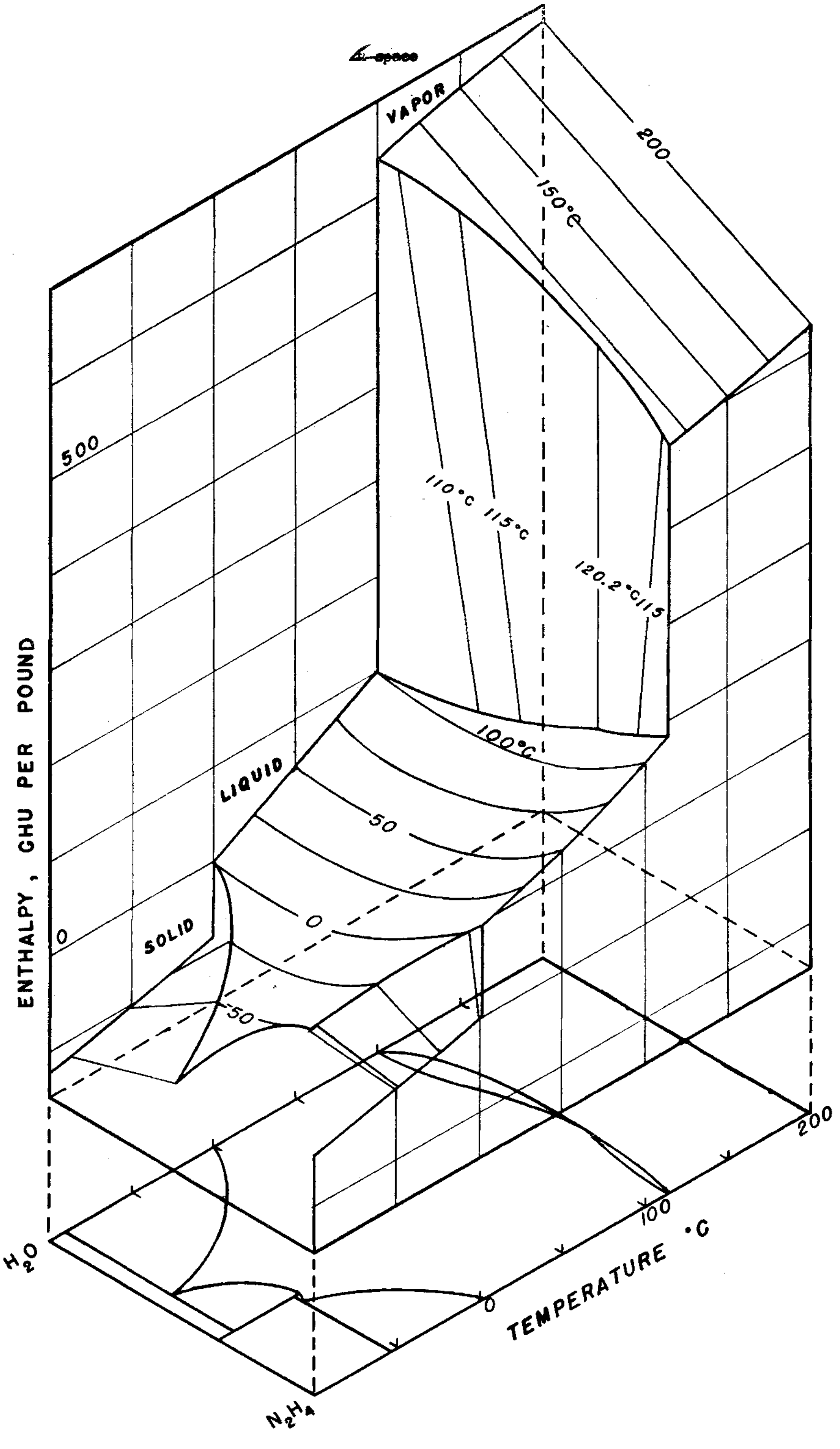


Fig. 5. Isometric View of H-x-t Surface in Space.

Phase Diagram for Binary Mixtures

Data on the phase relationships in the binary system are necessary if the enthalpy-concentration diagram is to include enthalpy data on the system in the solid and vapor phases. The data of Hill and Sumner (*15*) in the solid-liquid region and those of Björkman (*16*) and Uchida, Ogawa, and Yamaguchi (*17*) in the liquid-vapor region are the most recent measurements on the hydrazine-water system. They are shown in Figure 3. The system has one solid compound, $N_2H_4 \cdot H_2O$, which melts at —51.7°C., and an azeotrope containing 66.6 wt.% hydrazine, which boils at 120.2°C. at 1 atm. pressure. In the solid-liquid-equilibrium region the diagram shows that hydrazine hydrate forms eutectic compositions with both water and hydrazine and also it indicates that the solid hydrate is not soluble in either solid water (ice) or solid hydrazine.

Completion of the Diagram

The procedure for establishing isotherms throughout the liquid region was shown above. The liquid-region boundaries are determined from the phase diagram. In the two phase regions enthalpies are additive (no heat effect is observed on mixing equilibrium phases), and so isotherms in these areas are straight lines connecting the enthalpies of the two phases at the equilibrium temperature. Three phases in a two-component system at constant pressure occur at invariant temperatures on the phase diagram and appear as isothermal triangular areas on the enthalpy-concentration diagram with the corners of the triangle located at the enthalpy value of each phase at the invariant temperature.

Isotherms in the vapor region are straight lines since there is little or no heat effect observed on mixing nonreactive vapors. The solid region in this diagram is incomplete since no information is available on the heat capacity and heat of fusion or heat of formation of the hydrazine monohydrate solid.

Figure 4 is the complete diagram including solid, liquid, and vapor regions at 1-atm. pressure. Figure 5 is an isometric plot showing the H-x-t diagram of Figure 4 in space. It is not so useful for calculation purposes as is Figure 4, but it illustrates how the *H-t* diagrams for the pure substances and the system phase diagram fit together. Note that the *H-t* diagrams for the pure substances form the composition boundaries on the figure, and the phase diagram is the projection of all the phase boundaries onto the *t-x* plane.

In view of the approximations involved in Figures 1 and 2 and the scale of plotting used in Figure 4, it is probable that the errors in an enthalpy value read from Figure 4 may be as much as ± 2 C.h.u./lb. of solution; however, it is believed that the chart is sufficiently accurate for most engineering calculations.

AQUEOUS SODIUM CARBONATE

Sodium carbonate is a widely used industrial chemical. In 1948 the estimated national consumption was 4,880,000 short tons. Since most processes involving the manufacture and use of sodium carbonate are carried out in aqueous solution, the thermal properties of these solutions are of utmost importance. An enthalpy-concentration diagram is indispensable for calculating the amount of heat necessary to warm or cool batches of solutions and mixtures of solids and solutions.

Recently Kobe and Sheehy *(18)* reviewed and also collated the thermochemical data on sodium carbonate and its hydrates and solutions. Their results and the tabulations by Rossini et al. *(19)* for the heat of formation of the hydrates and the heat of solution of the anhydrous salt are in essential agreement. Kobe and Sheehy's data were used in the construction of Figure 6. The thermal properties of water were taken from Keenan and Keyes *(11)*.

The heat capacities of the monohydrate and septahydrate salts are unknown, but they have been estimated from the known heat capacities of the anhydrous and decahydrate salts on the assumption that the heat capacity of the various hydrates is directly proportional to the moles of water in the salt; thus

Na_2CO_3 (s)	26.38	
$Na_2CO_3 \cdot H_2O$ (s)	36.5	(est.)
$Na_2CO_3 \cdot 7H_2O$ (s)	97.1	(est.)
$Na_2CO_3 \cdot 10H_2O$ (s)	127.40	

An enthalpy-concentration diagram using the data sources discussed above is shown in Figure 6. As enthalpy changes at constant pressure are heat quantities, the diagram may be used at atmospheric pressure to find the resulting temperature for any adiabatic mixing process occurring in this system or the amount of heat (*a*) to be removed in any sodium carbonate crystallization process, (*b*) to change the temperature of any mixture in this system, and (*c*) to keep any solution process in this system at constant temperature. Positive enthalpy changes mean that heat is gained by the system and negative values mean heat lost from the system.

AQUEOUS GLYCERINE

Glycerine and its aqueous solutions are used in the quick-freeze and refrigerating industries. They are particularly useful in the food industry because glycerine is edible and has an agreeable, sweet taste; consequently accidental contamination of food with the refrigerant is not completely objectionable. Glycerine solutions are also used in cold plates to act as a thermal buffer. Hospital ice bags filled with a 10 to 15% solution can be permanently sealed and frozen in a refrigerator to be used when needed. The thermal buffering capacity of an aqueous glycerine mixture is found by subtracting the enthalpy of the system at its original temperature from its enthalpy at the final temperature.

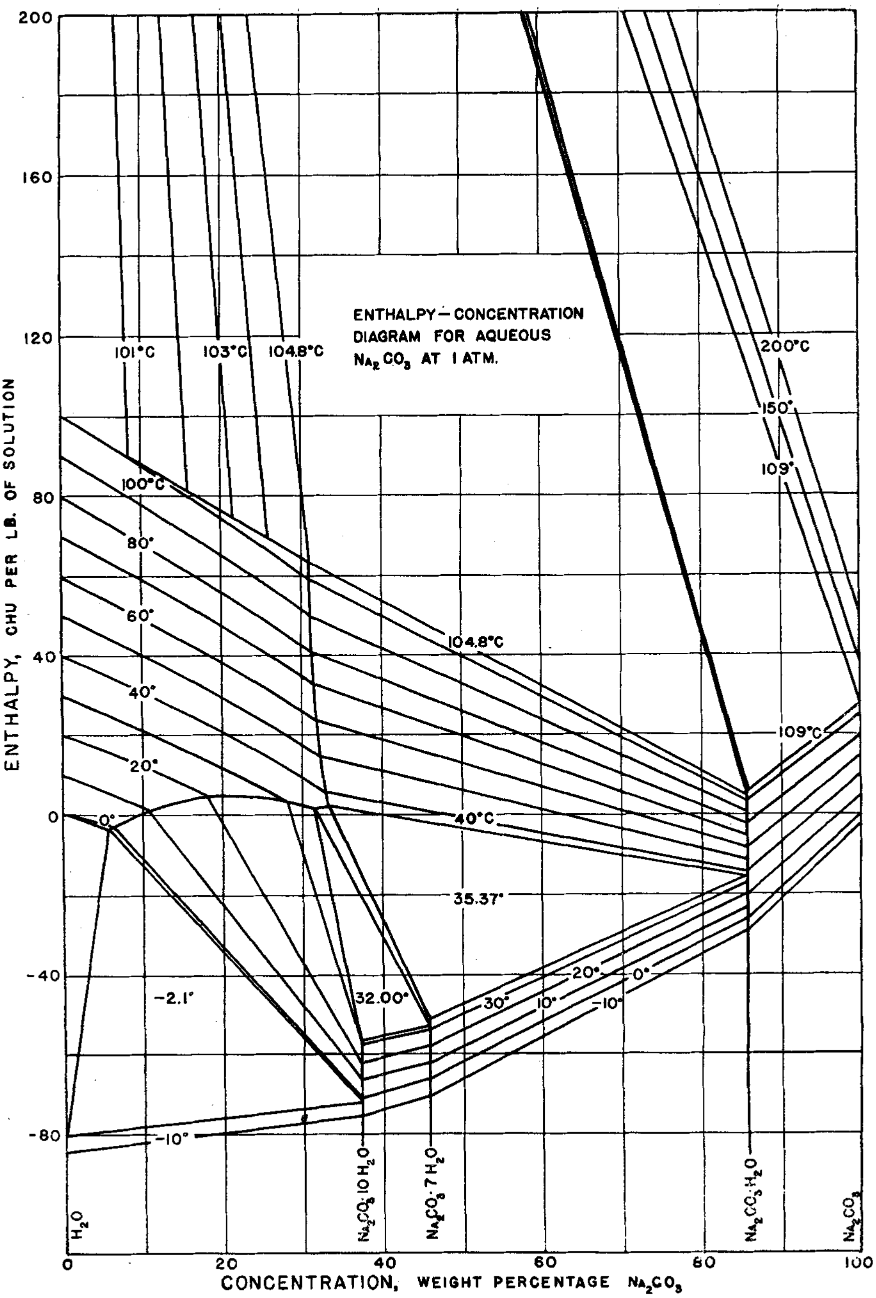


FIG. 6. ENTHALPY-CONCENTRATION DIAGRAM FOR SODIUM CARBONATE AND WATER AT 1 ATM. REFERENCE ENTHALPIES ARE ZERO FOR LIQUID WATER AND SOLID SODIUM CARBONATE AT 0°C.

The reference conditions for the enthalpy-concentration diagram in Figure 7 are zero enthalpies for pure liquid water and solid glycerine at 0°C. The enthalpy data for water were obtained from Keenan and Keyes (*11*) and Hodgman (*20*). The enthalpy data for glycerine were calculated from heat-capacity data from Hodgman (*20*). Heat-of-solution data for the system at 20°C. were obtained from the International Critical Tables (*21*). Heat-capacity data for aqueous solutions are given by Perry (*22*) at 15° and 32°C. and by Gucker and Marsh (*23*) down to —30°C. Gucker and Marsh give heat-capacity data in the two-phase (solid-liquid) region and also a tabulation of the heat required to heat 1 lb. of glycerine-water mixture from various temperatures to 0°C. From these data and the solid-liquid phase diagram of Lane (*24*) the diagram was extended to the eutectic temperature. Below the eutectic temperature the phases are pure solid water and solid glycerine and the isotherms are straight lines connecting the enthalpies of the pure materials.

Isotherms above 20°C. were constructed by adding the temperature integral of the heat capacity to the 20°C. value. In this manner isotherms up to the boiling point may be constructed. Heat-capacity data at 25°C. and normal boiling temperatures of the aqueous solutions were obtained from Miner and Dalton (*25*).

Figure 7 gives the diagram complete in the solid and liquid regions. The liquid-vapor and vapor regions are not included because sufficient experimental data are not available to establish this portion of the diagram.

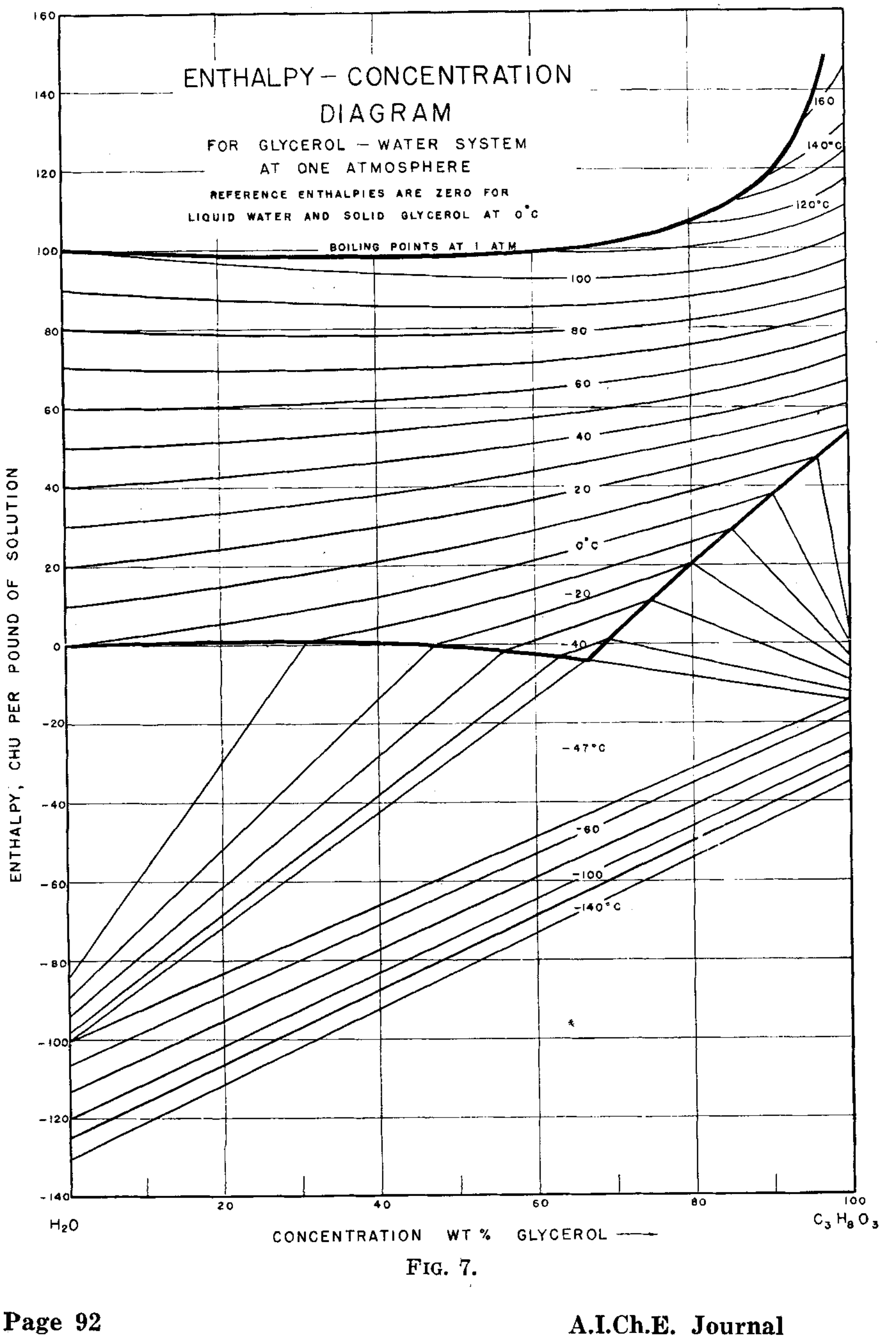


FIG. 7.

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